Solar Fuels – Sulfur and Ferrites and Thermochemical Storage

Examples carried out by DLR and General Atomics

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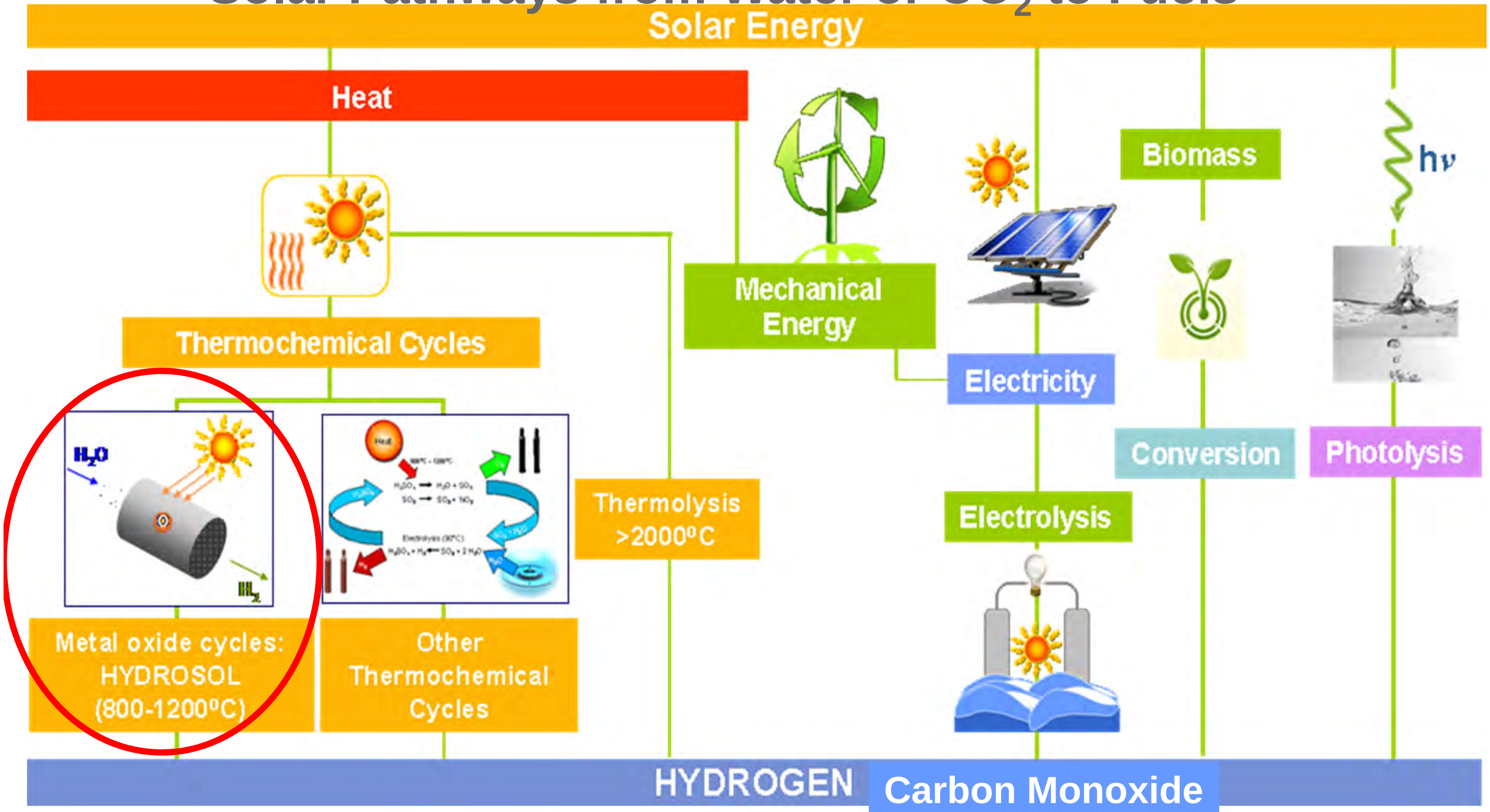
Solar Pathways from Water or CO_2 to Fuels



Promising and well researched Thermochemical Cycles

	Steps	Maximum Temperature (°C)	LHV Efficiency (%)
Sulphur Cycles			
Hybrid Sulphur (Westinghouse, ISPRA Mark 11)	2	900 (1150 without catalyst)	43
Sulphur Iodine (General Atomics, ISPRA Mark 16)	3	900 (1150 without catalyst)	38
Volatile Metal Oxide Cycles			
Zinc/Zinc Oxide	2	1800	45
Hybrid Cadmium		1600	42
Non-volatile Metal Oxide Cycles			
Iron Oxide	2	2200	42
Cerium Oxide	2	2000	68
Ferrites	2	1100 – 1800	43
Low-Temperature Cycles			
Hybrid Copper Chlorine	4	530	39

Efficiency comparison for solar hydrogen production from water (Siegel et al., 2013)*

Process	T [°C]	Solar plant	Solar-receiver + power [MW_{th}]	η T/C (HHV)	η Optical	η Receiver	η Annual Efficiency Solar – H_2
Elctrolysis (+solar-thermal power)	NA	Actual Solar tower	Molten Salt 700	30%	57%	83%	13%
High temperature steam electrolysis	850	Future Solar tower	Particle 700	45%	57%	76,2%	20%
Hybrid Sulfur-process	850	Future Solar tower	Particle 700	50%	57%	76%	22%
Hybrid Copper Chlorine-process	600	Future Solar tower	Molten Salt 700	44%	57%	83%	21%
Metaloxide two step Cycle	1800	Future Solar dish	Particle Reactor < 1	52%	77%	62%	25%

**N.P. Siegel, J.E. Miller, I. Ermanoski, R.B. Diver, E.B. Stechel, Ind. Eng.Chem. Res., 2013, 52, 3276-3286.*

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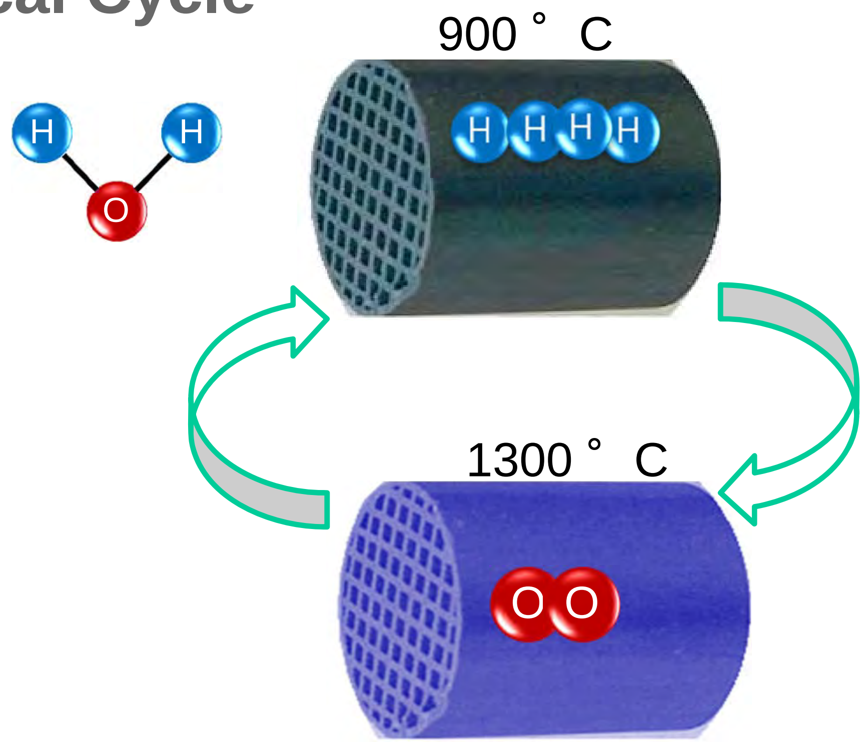
HYDROSOL concept for running the 2 Step Thermochemical Cycle

1. Water Splitting

$H_2O + MO_{red} \rightarrow MO_{ox} + H_2$

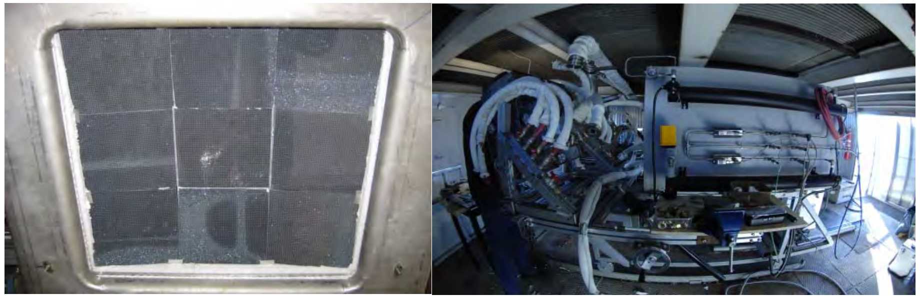
2. Regeneration

$MO_{ox} \rightarrow MO_{red} + ½ O_2$



Net Reaction: $H_2O \rightarrow H_2 + ½ O_2$

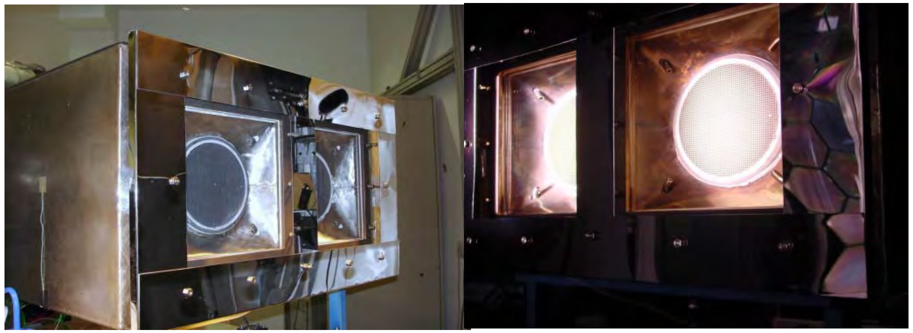
Hydrosol technology scale-up



2008:

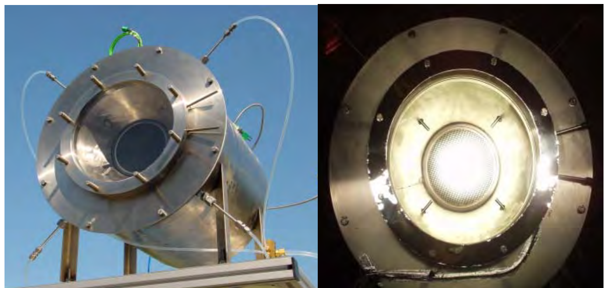
Pilot reactor (100 kW)

PSA solar tower



2005:

Continuous H_2 production



2004:

First solar thermochemical

H_2 production

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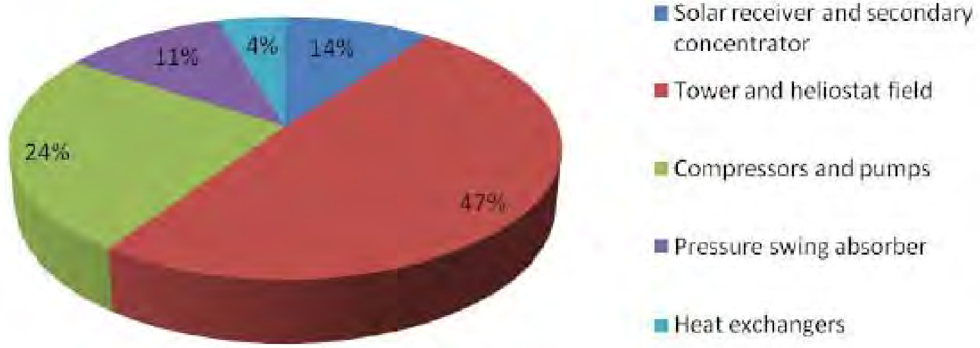
Solar fuels from thermochemical cycles- HYDROSOL 3D project- Main results Economic analysis of the demonstration plant

- Demonstration plant thermal energy input: 1 MW
- Cost calculation of the new designed reactor was carried out.
- Cost calculation of the overall process units was performed.
- More than half of process investment results from the solar system.

Component	Number of units	Cost per unit [€]	Total Cost [€]
Quartz plates	14	600	8400
Reactor modules	14	3000	42000
Secondary concentrator	14	12000	168000

Solar part incl. receiver-reactor[€]	1,406,847
Pressure swing absorber [€]	265,000
Compressors and pumps [€]	584,054
Heat exchangers [€]	110,493
Total cost [Mio. €]	**2.366**



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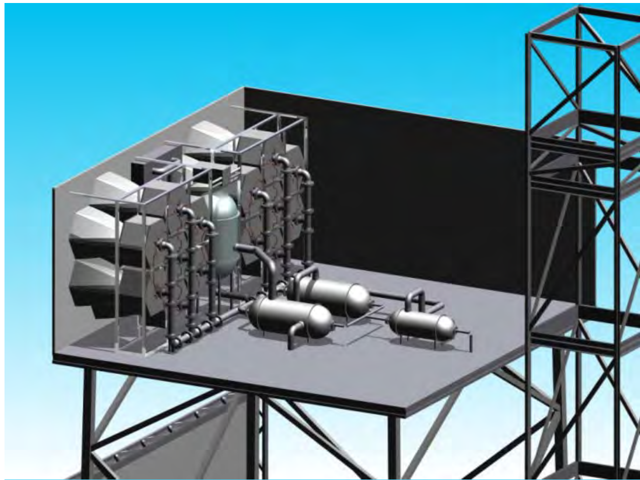
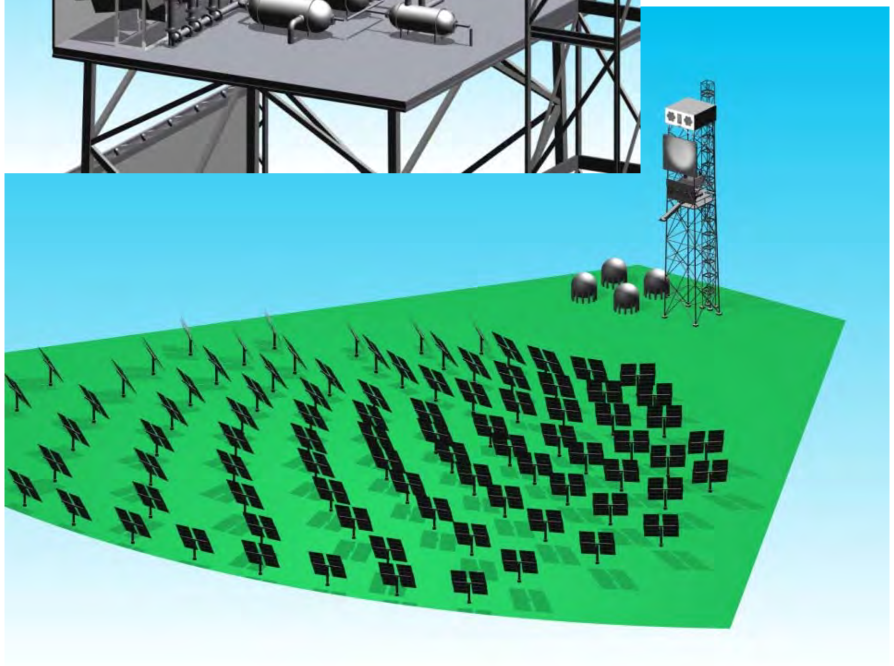
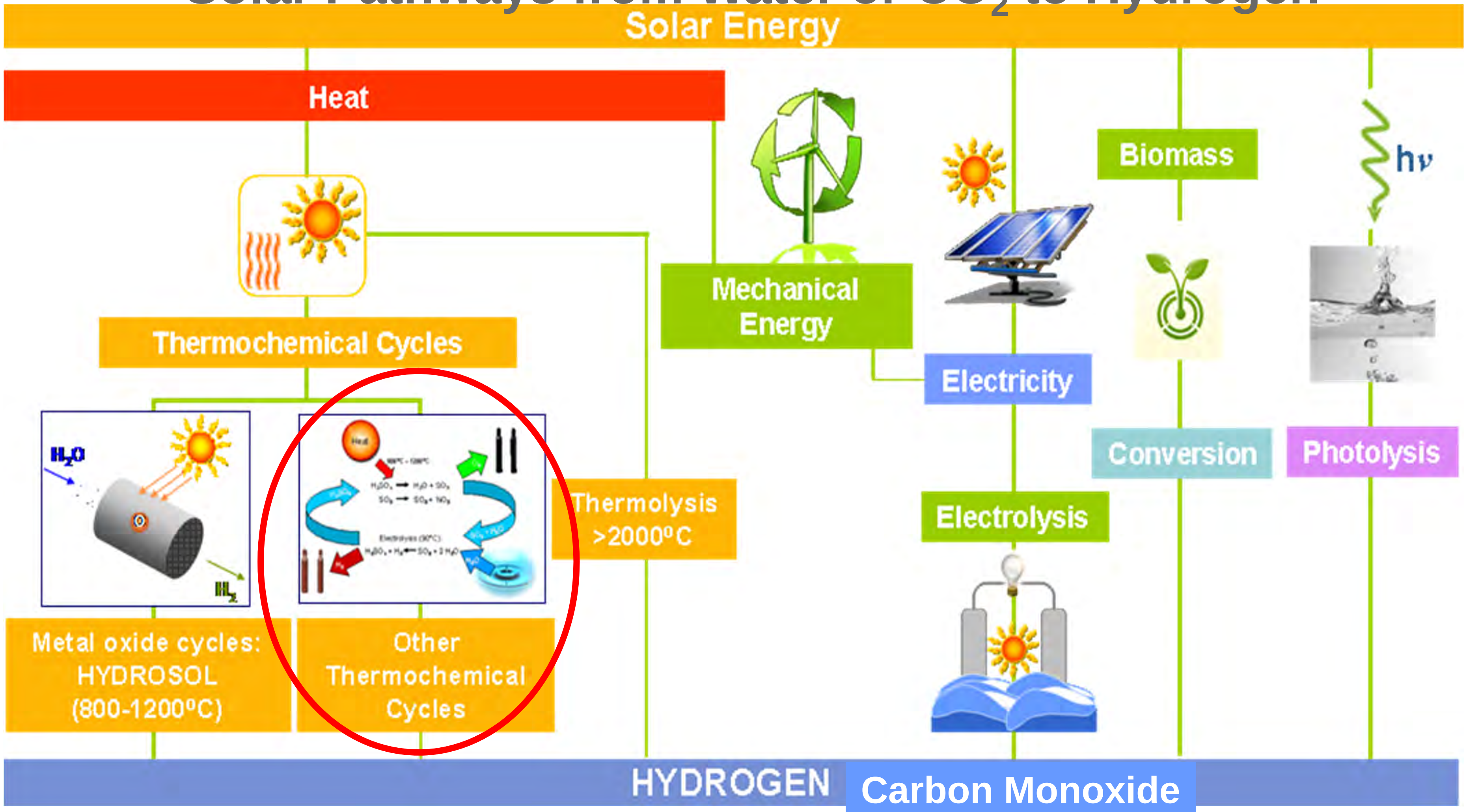
Hydrosol Plant - Design for CRS tower PSA, Spain

- European FCH-JU project
- Partner: APTL (GR), HELPE (GR), CIEMAT (ES), HYGEAR (NL)
- 750 kW_{th} demonstration of thermochemical water splitting
- Location: Plataforma Solar de Almería, Spain, 2015
- Use of all heliostats
- Reactor located on the CRS tower
- Storage tanks and PSA on the ground

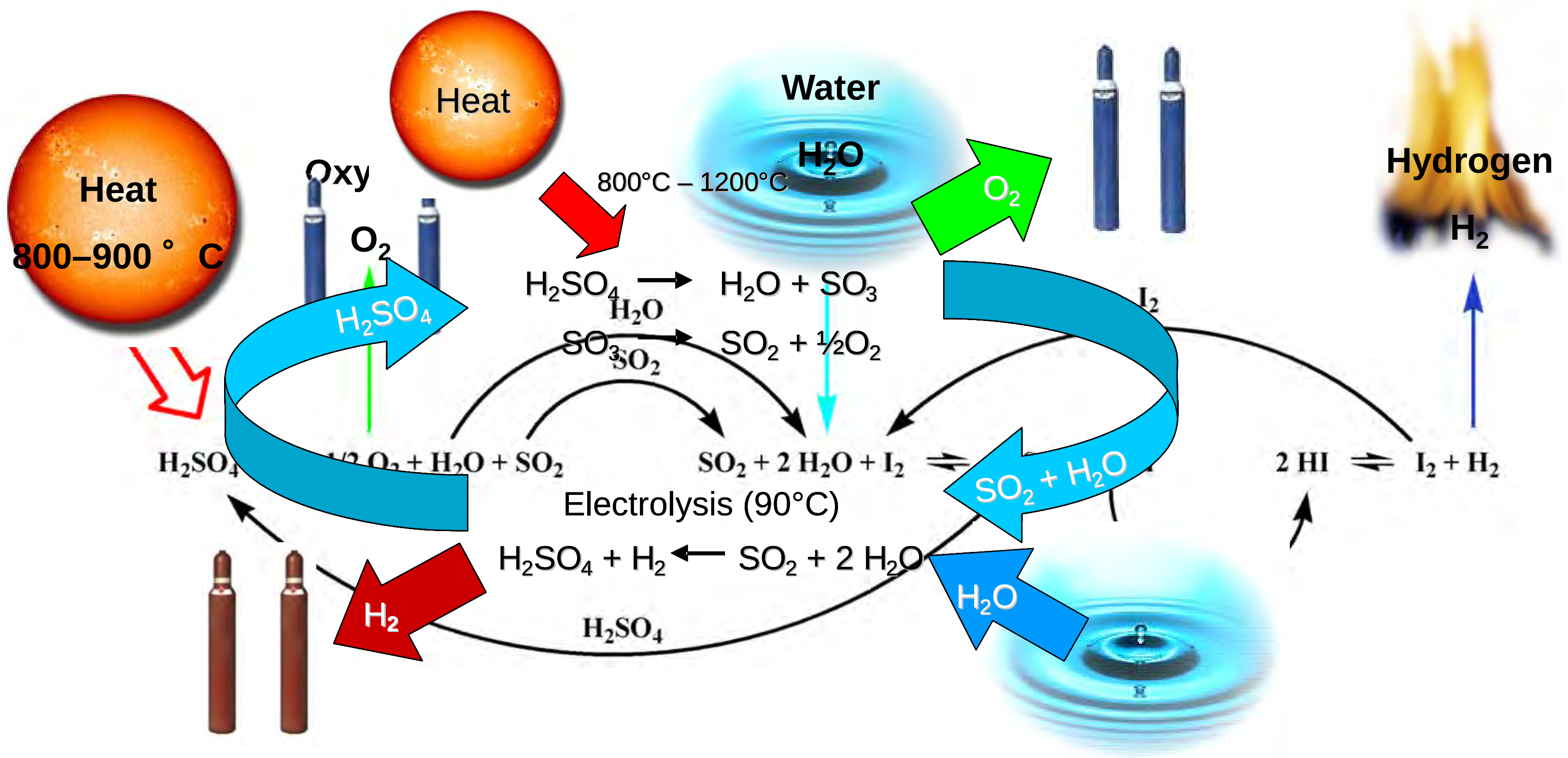




Solar Pathways from Water or CO_2 to Hydrogen



Hybrid Sulphur Cycle
Sulphur-Iodine Process



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H_2SO_4 decomposition in 2 steps

1. Evaporation of liquid sulfuric acid (400° C)

$$H_2SO_4 \rightleftharpoons SO_3 + H_2O$$

2. Dissociation of sulfur trioxide (850° C)

$$SO_3 + H_2O \rightleftharpoons SO_2 + \tfrac{1}{2}\,O_2 + H_2O$$

Absorbers:

SiSiC foam

SiSiC honeycomb

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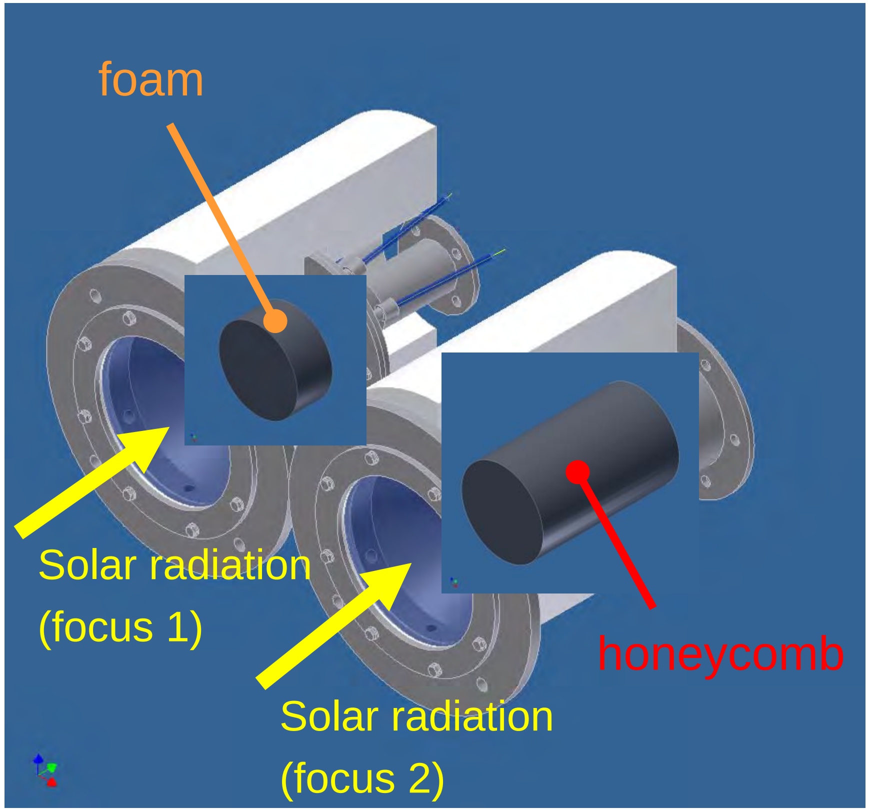
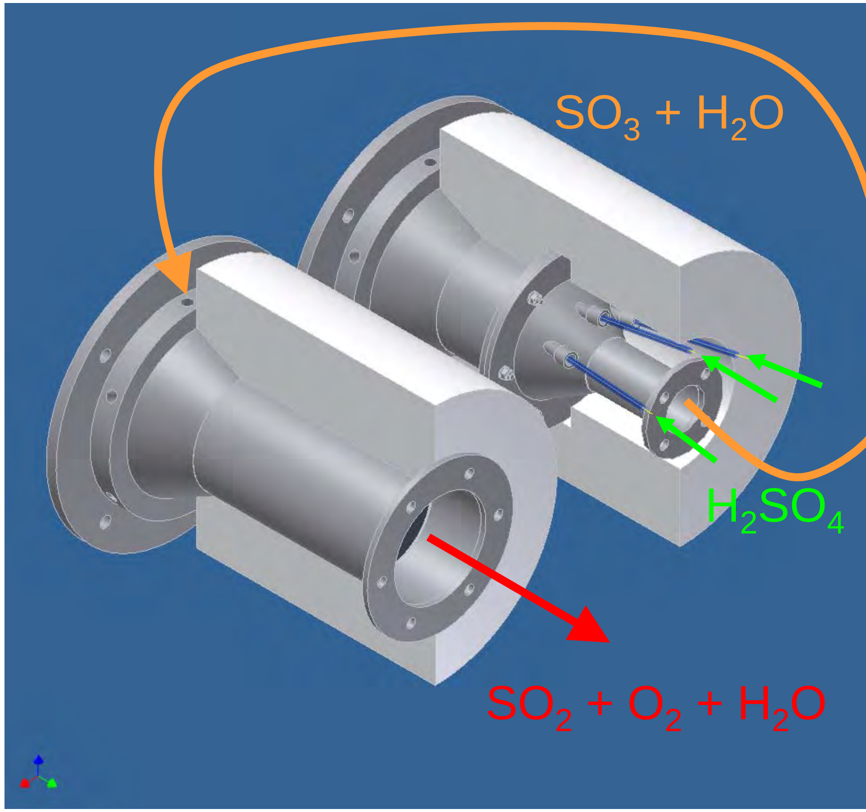
Design of multi-chamber solar reactor

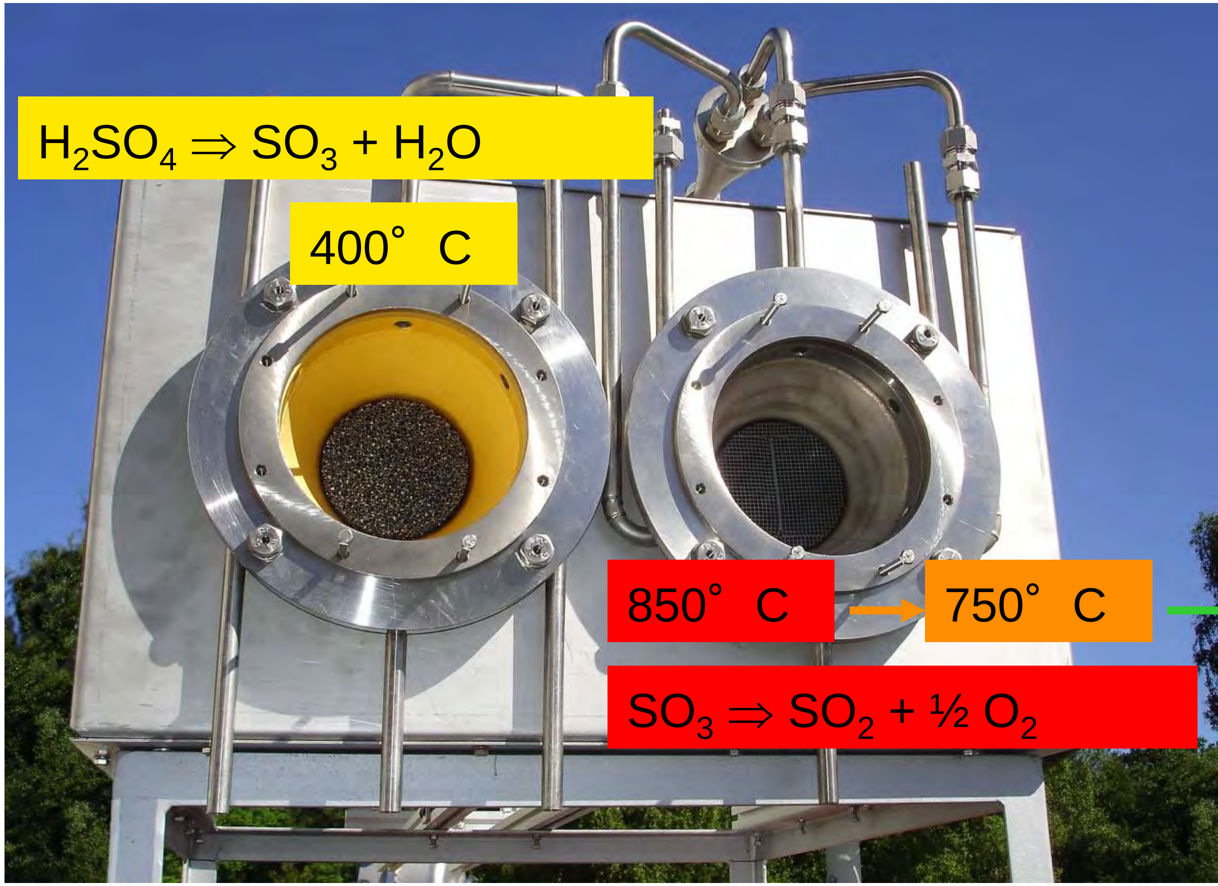


Front view of evaporator (left) and decomposer



Rear view

Solar reactor for sulfuric acid decomposition



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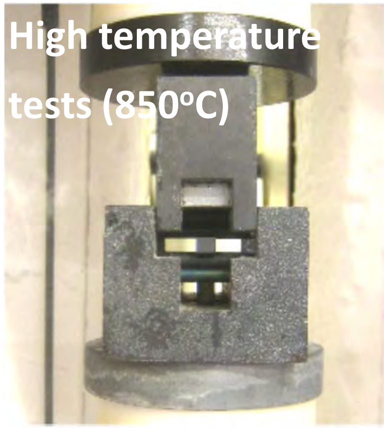
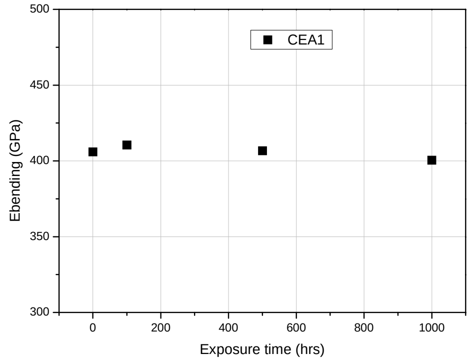
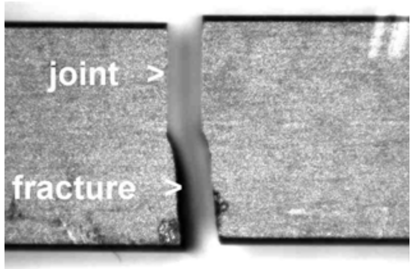
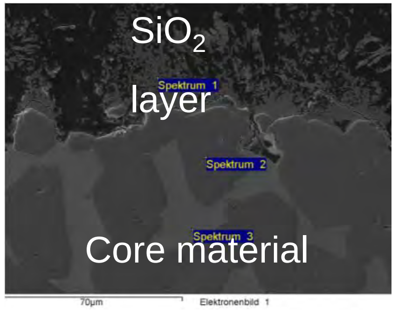
Stability of construction materials







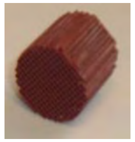


- Performance of long-term corrosion campaigns (SO_2, SO_3 rich, boiling H_2SO_4) and post-exposure mechanical testing and inspection
- mainstream materials SiC-based as well as brazed samples
- SiC based materials retained suitable for the intended application since they are not affected significantly by the SO2-rich, SO3-rich and boiling sulphuric acid exposures.

Advanced catalysts and coatings for H_2SO_4 decomposition

– 'In-house' synthesized materials (metal oxide based) with high catalytic activity in terms of SO_2 production from H_2SO_4:

– Coating of active materials in small- & large-scale SiSiC monoliths or fragments



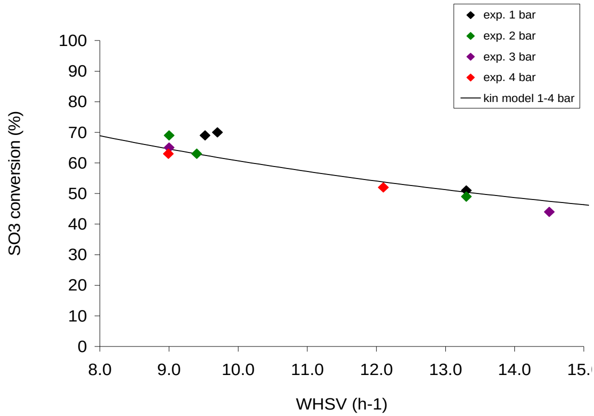
– Satisfying stability of samples coated with 'in-house' materials under 'long-term' operation

– Derivation of an empirical kinetic model

– Evaluation of the employed materials chemical stability

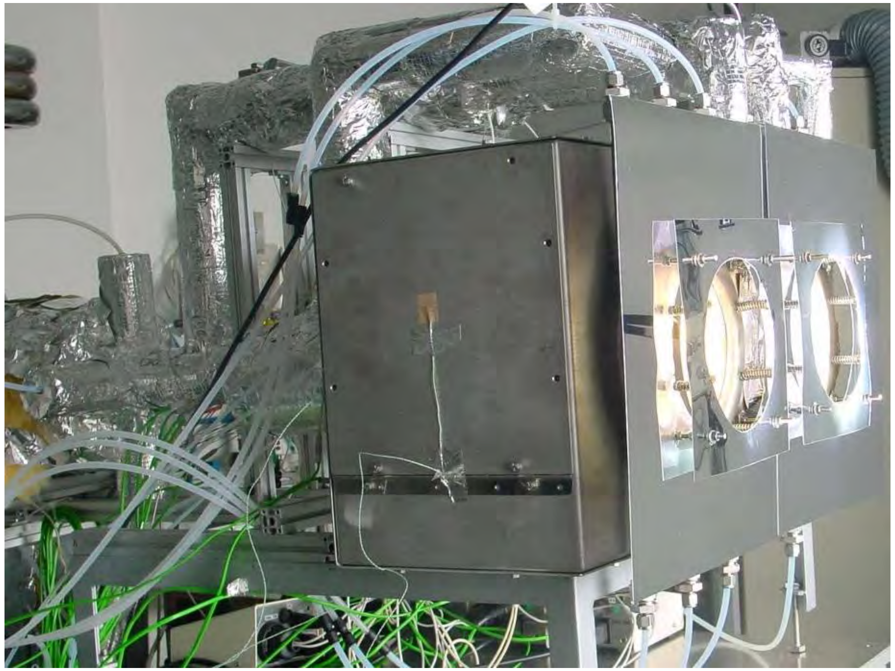
– Extraction of an SO_3 dissociation mechanism

– CrFe oxide identified as the most suitable catalyst

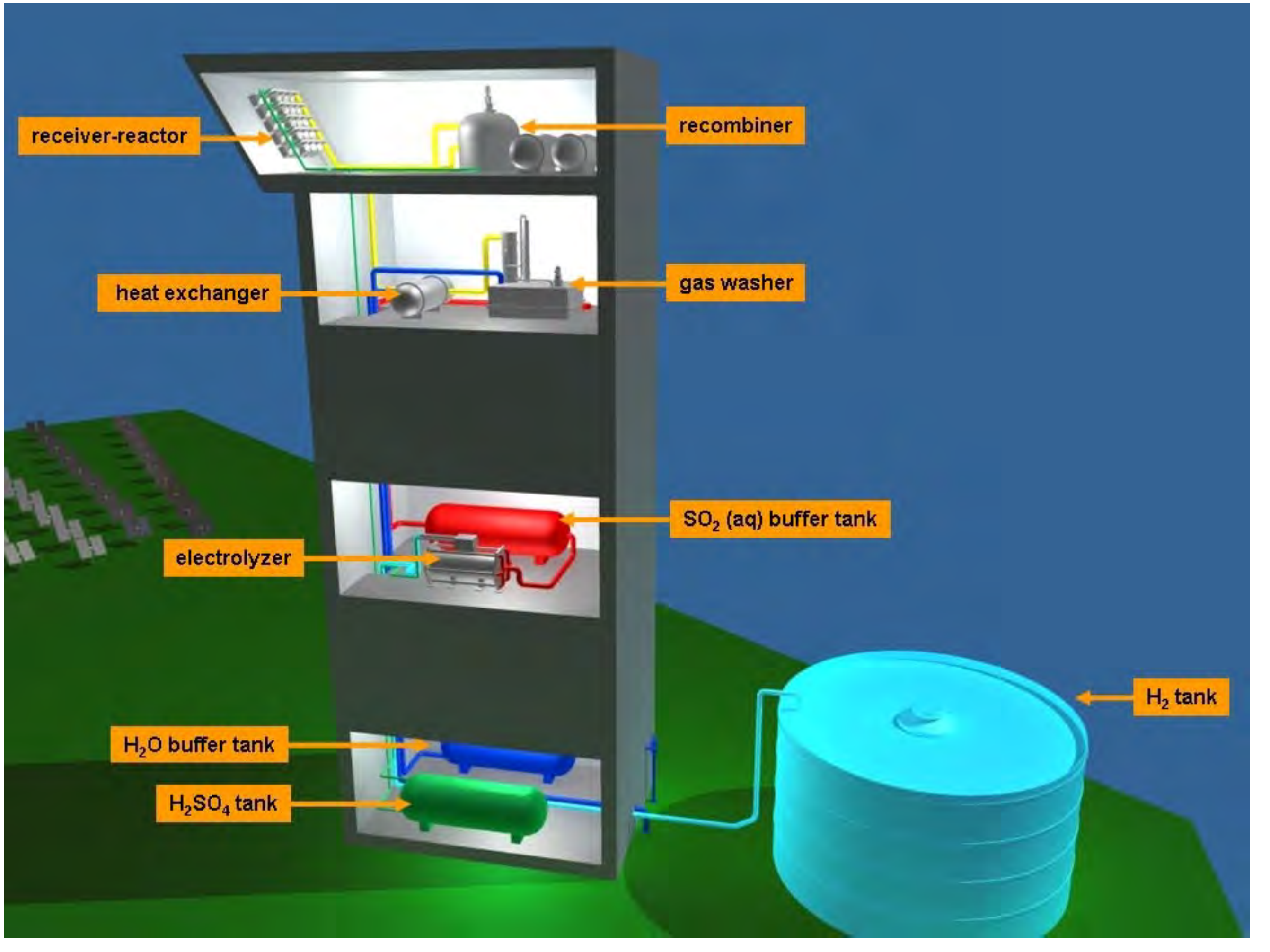


Karagianakis et al, IJHE 2011/2012; Giaconia et al, IJHE 2011

Operation in our solar furnace in Cologne



Implementation into a Solar Tower



Thermochemical Energy Storage

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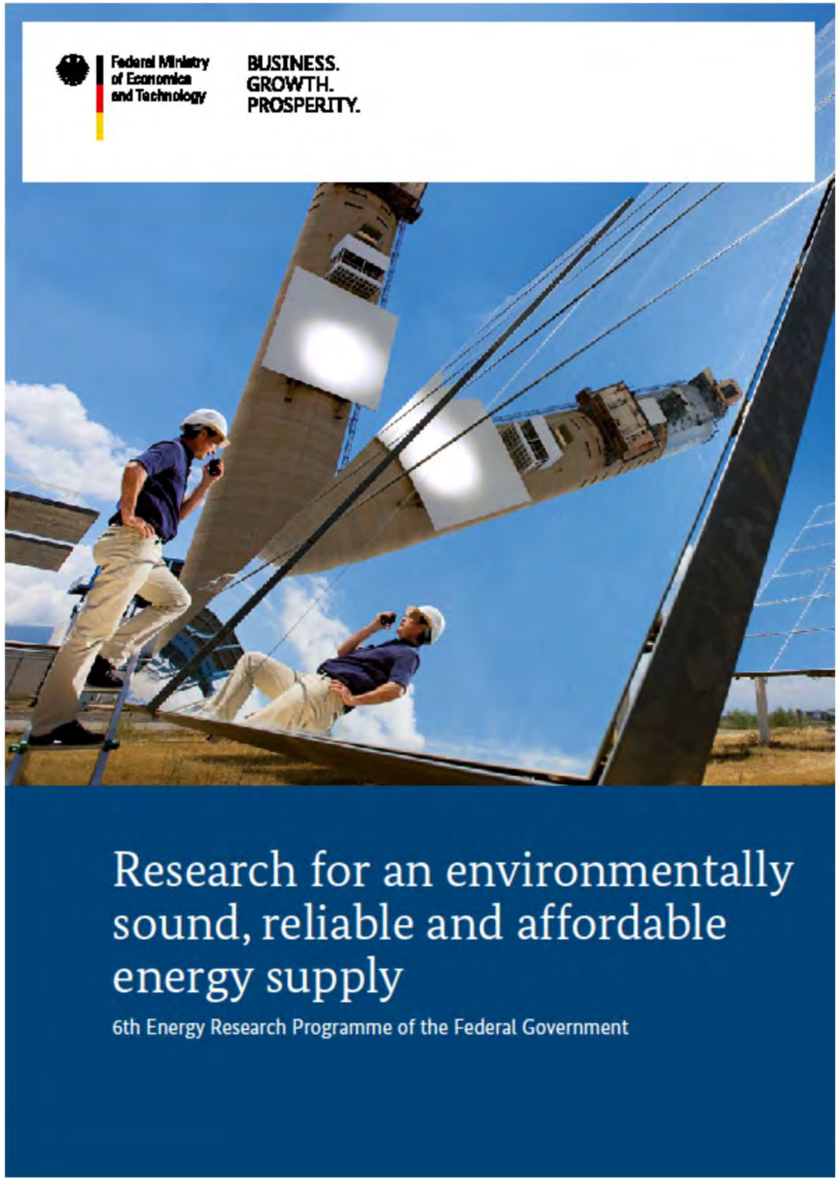
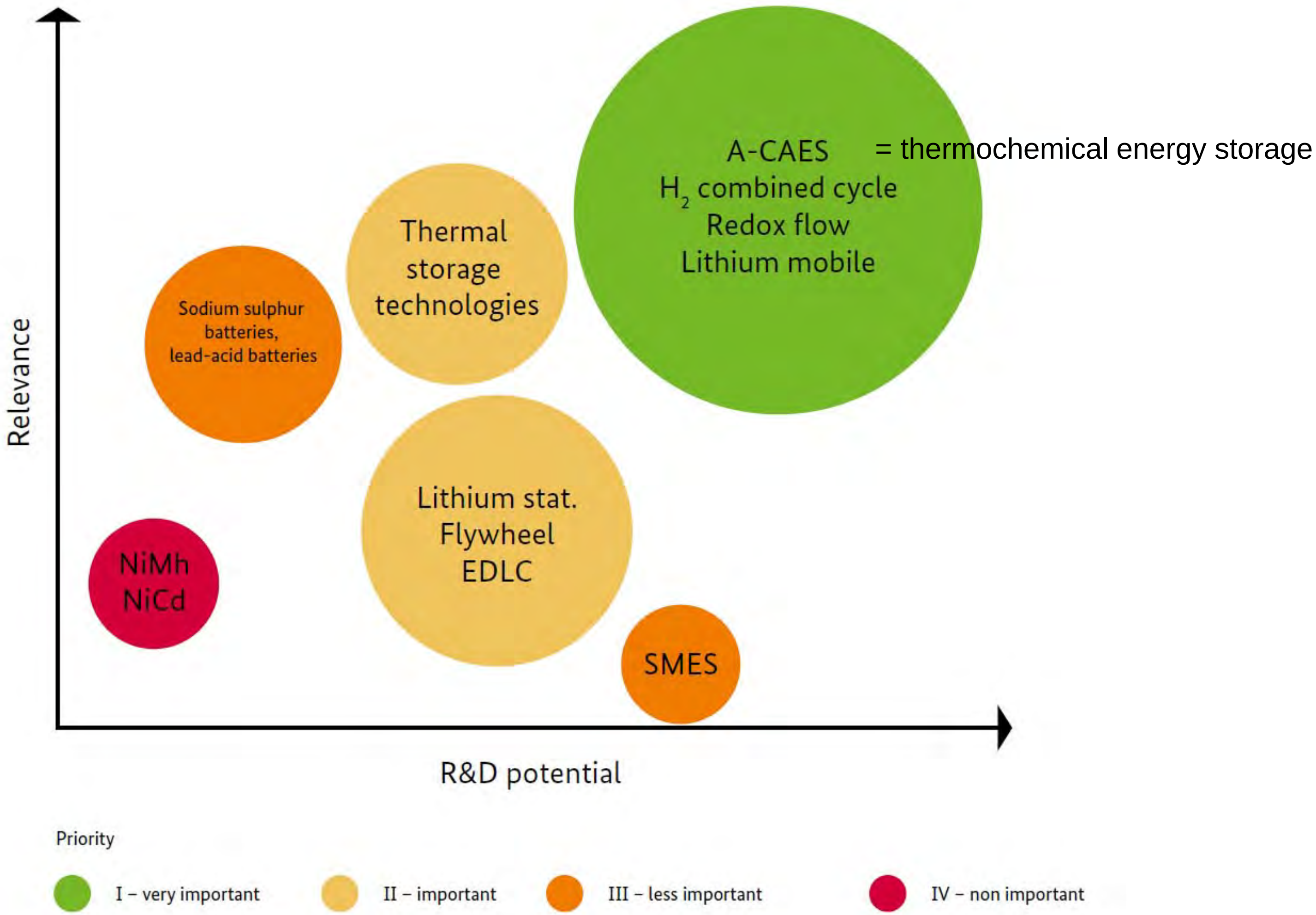
Programs in Germany

- 6th Energy Research Programme (3.5 billion euros for the period 2011-2014).

- The Programme focuses on key topics relating to the restructuring of Germany's energy supply, i.e.
    - renewable energies,
    - energy efficiency,
    - storage and grids.



6th Energy Reserach Programme



Thermochemical heat storage can provide very high energy storage densities

Technology	Energy Density (kJ/kg)
Gasoline	45000
Sulfur	12500
Cobalt Oxide	850
Molten Salt (Phase Change)	230
Molten Salt (Sensible)	155
Lithium Ion Battery	580
Elevated water Dam (100m)	1

- **High energy densities with low storage cost**
- **Ambient and long term storage**
- **Transportability**

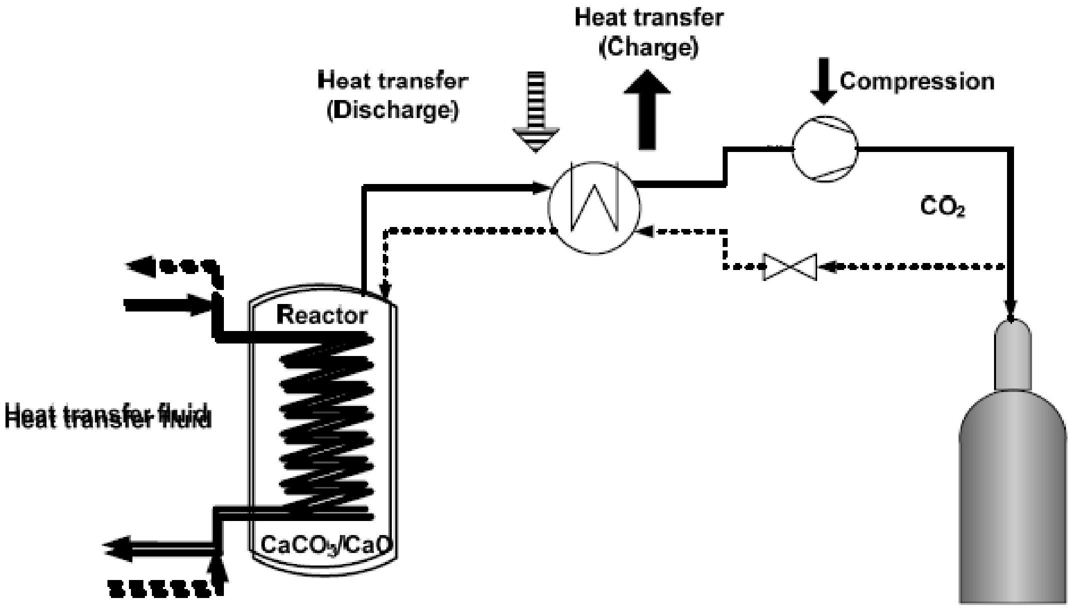
Reversible Gas-Solid-Reactions

- High storage density
- Lossless long-term storage possible
- Possible heat transformation
- Large temperature range (RT to > 1000 °C)
- Decoupling of storage capacity loading power
- Cost efficient storage materials

- Reactions:
  - Dehydratation: $CaCl_2*6H_2O = CaCl_2 + 6\ H_2O$
  - Metalhydroxide/Metaloxide: $Ca(OH)_2 = CaO + H_2O$
  - Redox cycles of Metaloxides: $2\ MnO_2 = Mn_2O_3 + ½\ O_2$

Thermo-Chemical energy storage - system

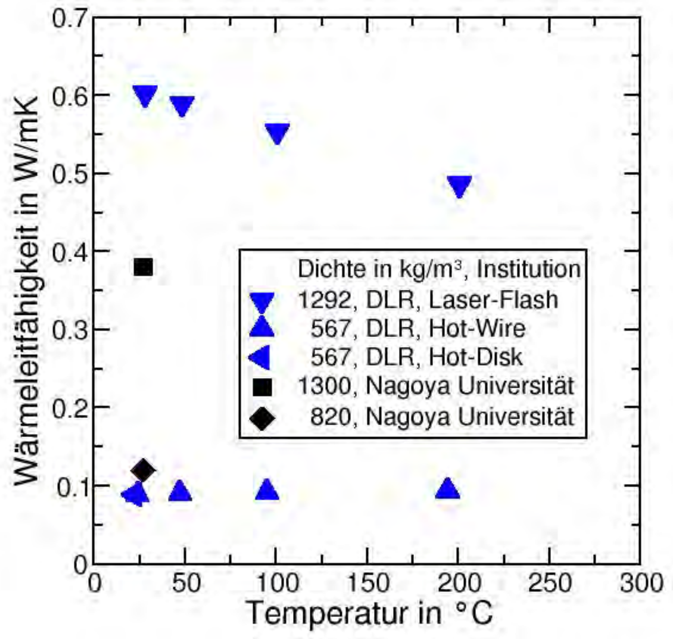
- Complex system, storage of gaseous reactant necessary
- Additional energy required (for compression)



Thermo-Chemical energy storage - material

- **Low thermal conductivity** of powder bed
- Thermal power?
- Reactor design

- **Material costs**
  - Amount of „useful“ cycles determines the amortization periode
    - Seasonal storage
    - Day / Night storage
    - Continuous operation (sorption system)



F. Schaube et al., High Temperature TC Heat Storage for CSP using Gas-Solid Reactions, Proceedings of SolarPaces 2010, Perpignan, France (2010)

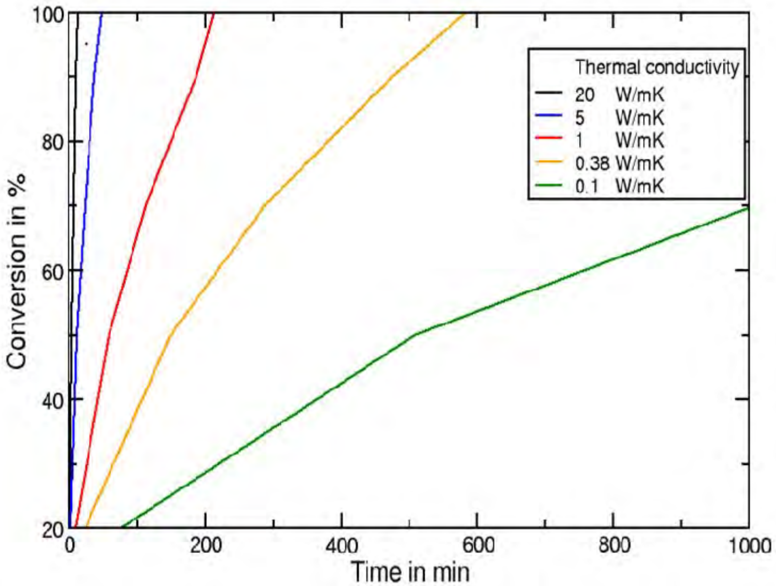
Key factors: Development of reactor systems Process integration

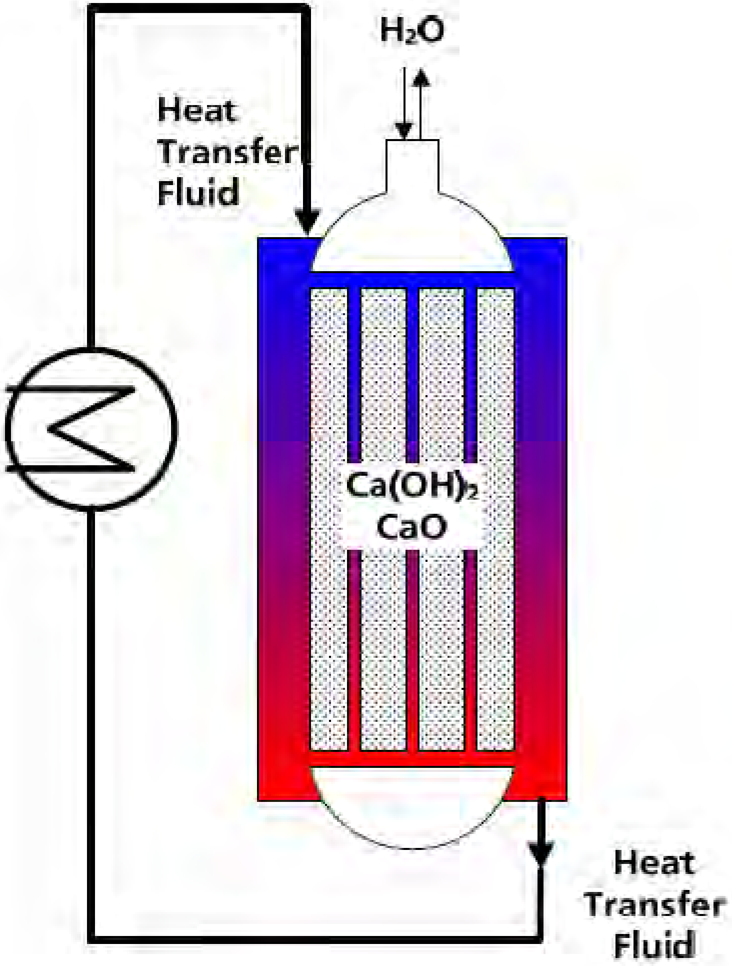
Current activites on Gas-Solid Reactions for heat applications at DLR:

- Competence Center for Ceramics and Storage in Energy Research CeraStorE
- Development of reactor systems:
  - Concept of direct heat transfer
  - $CaO/Ca(OH)_2$
  - Metaloxide Redoxcycles
  - Sulfur Cycles

CaO/Ca(OH)$_2$ system

- Temperatur range: 400 – 600 °
  - CSP plants
- Bed with **low thermal conductivity**

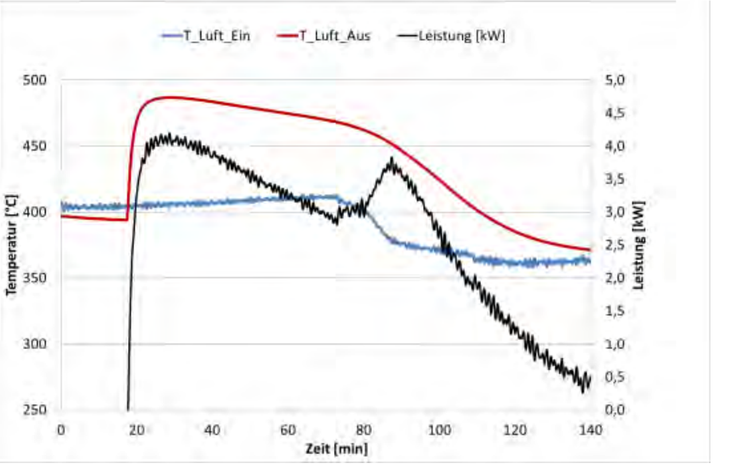


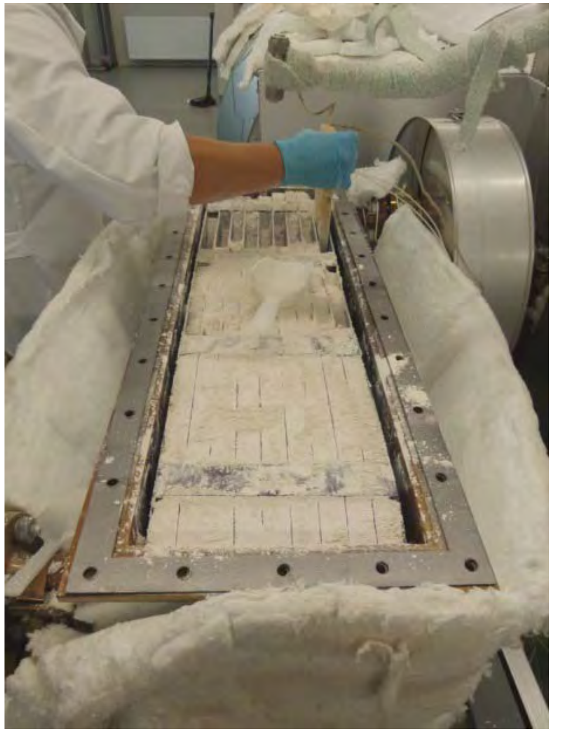


F. Schaube et al., High Temperature TC Heat Storage for CSP using Gas-Solid Reactions, Proceedings of SolarPaces 2010, Perpignan, France (2010)

$CaO/Ca(OH)_2$

- Principle successfully demonstrated in a 10 kW plant in the CeraStorE





RESTRUCTURE

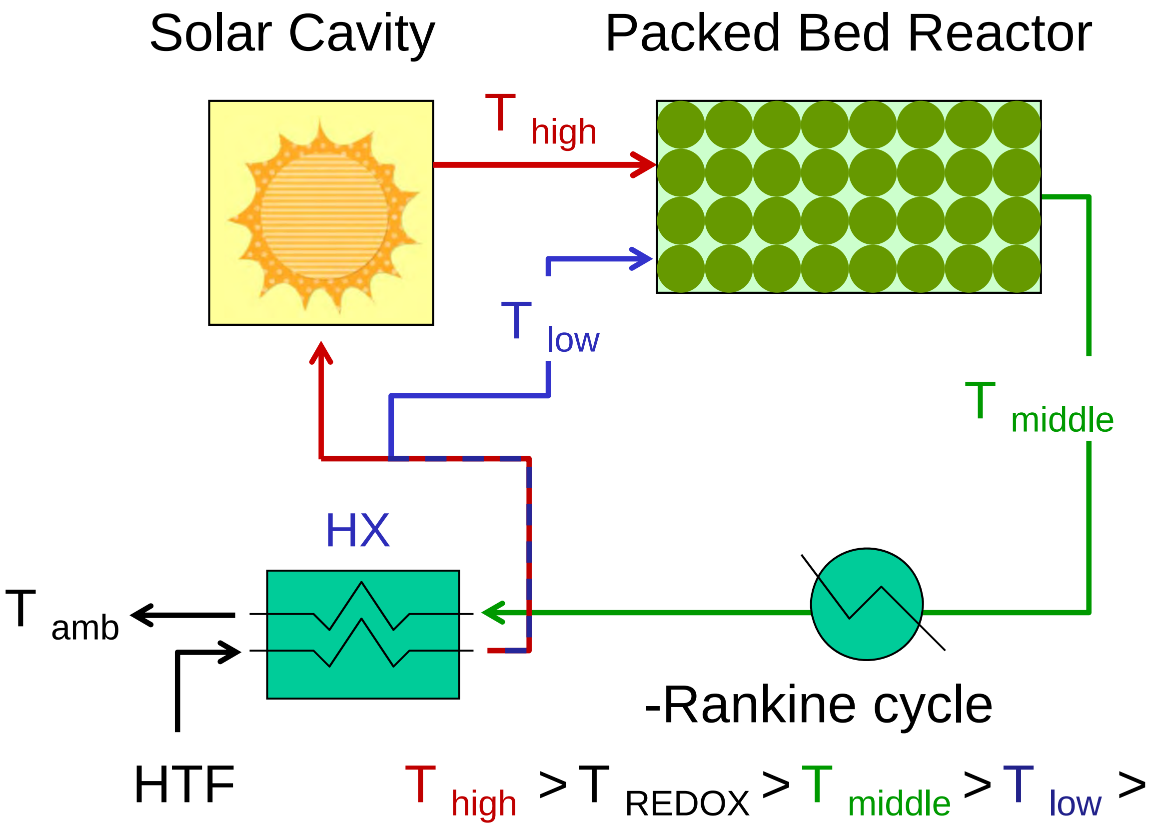
- FP 7 European Project 2012 - 2016
- Redox Cycles with fixed structures: Honeycombs or foams
- Mixed-iron-oxides-based redox materials
- Demonstration of operation in the temperature range of a solar tower: 900-1500° C
- Demonstration of a solar pilot plant of 100 kW
- Identification of investment and operational cost of a 1.5MWe demo plant incorporating the particular TES system and comparison to other storage options.
- Presentation of a suitable strategy for the introduction of the technology into the market.

General Atomics led two thermochemical energy storage projects that have been supported by the USA Department of Energy - DOE

1. **Solid Oxide Based Thermochemical Heat Storage***
   (DOE Advance TES program DE-FG-36-08GO18145)
2. **Sulfur Based Thermochemical Heat Storage for Baseload***
   (DOE Baseload program DE-EE0003588)

*** Project partner: German Aerospace Center (DLR)**

A pair of solid oxide REDOX reactions were used to store and release heat



$T_{high} > T_{REDOX} > T_{middle} > T_{low} >> T_{amb}$

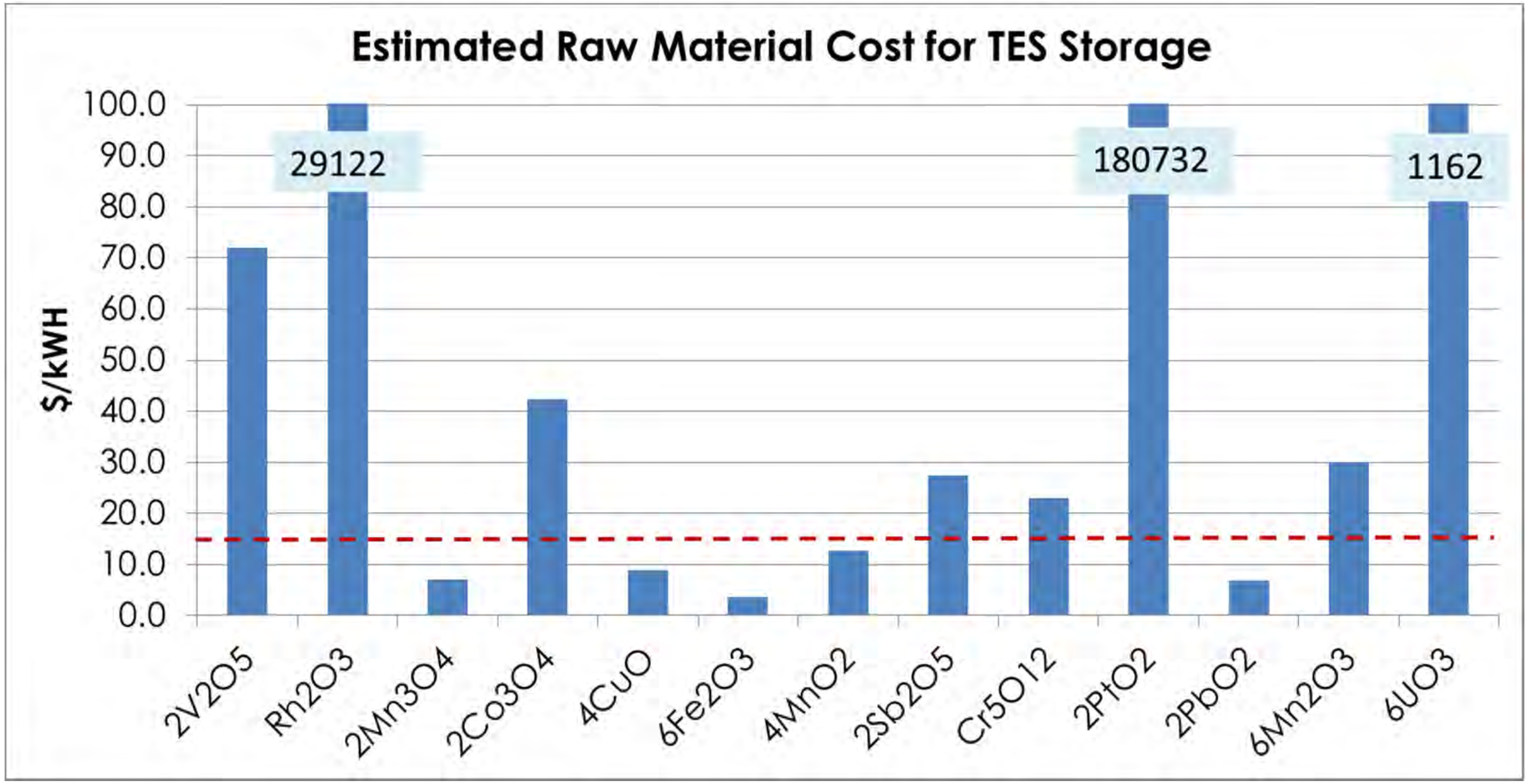
- **The heat transfer fluid (HTF) is also the reactant e.g. Air (O_2), CO_2 & H_2O**
- **Open System – no storage of HTF: oxides**
- **Closed System – HTF storage required: carbonates, hydroxides**

$MO_{2x+1} \rightarrow MO + xO_2$ ⟶ -On sun$_{endo.}$ (charge)

$MO + xO_2 \rightarrow MO_{2x+1}$ ⟶ -Off sun$_{exo.}$ (discharge)

Preliminary economics can be estimated through energy related costs

- **Energy related costs include raw materials, storage and process cost etc.**



DOE target

- **Low raw material cost required for large scale use**

REDOX of solid oxide is applicable to thermochemical energy storage for CSP

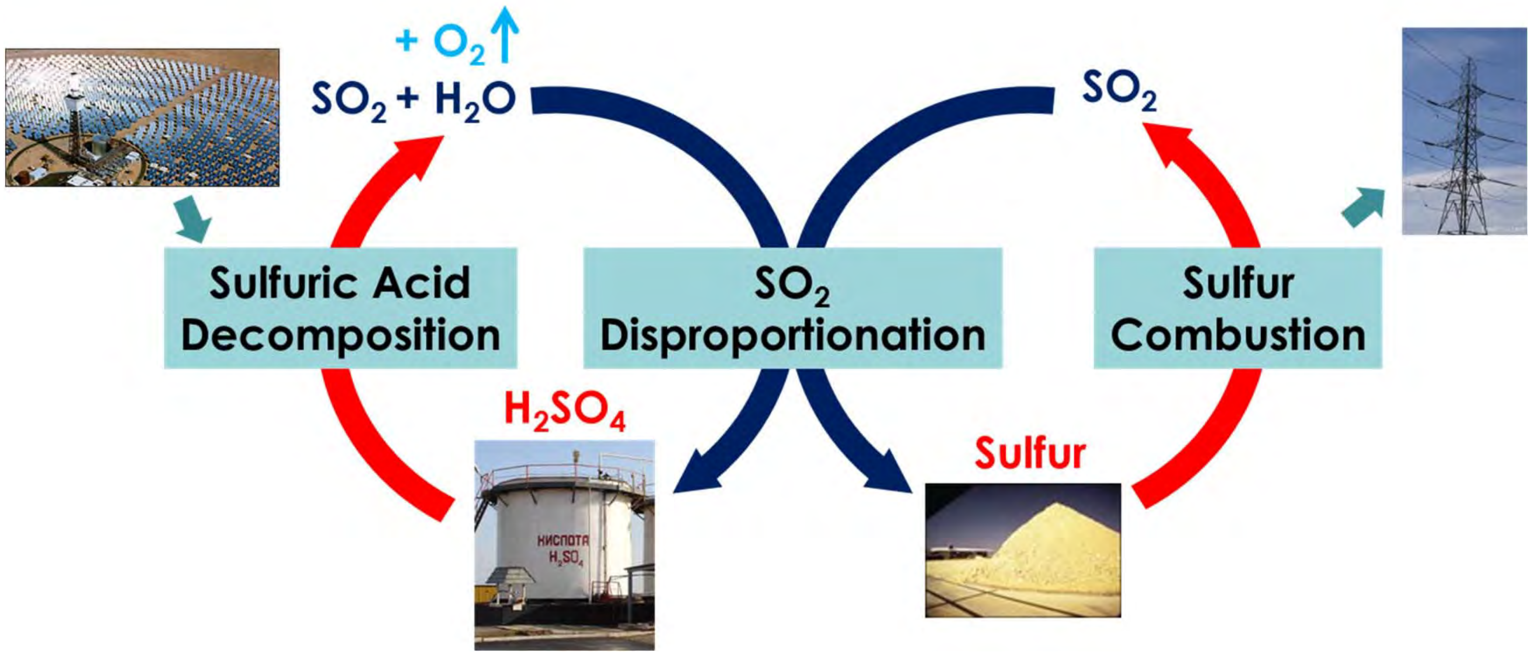
- Mixed oxides greatly improves REDOX kinetics and cycle repeatability
- Materials cost is the main driver of TES economics
- A moving bed reactor is required to minimize parasitic cost

DOE Metric	Unit	2015	Mn-Fe	Co-Al
Storage Cost	$/kWh	15	15-35	50-100
LCOE	$/kWh	0.06	0.09-0.11*	0.13-0.17*
Efficiency	%	93	>93	>93

*SAM (NREL) using 2010 costs

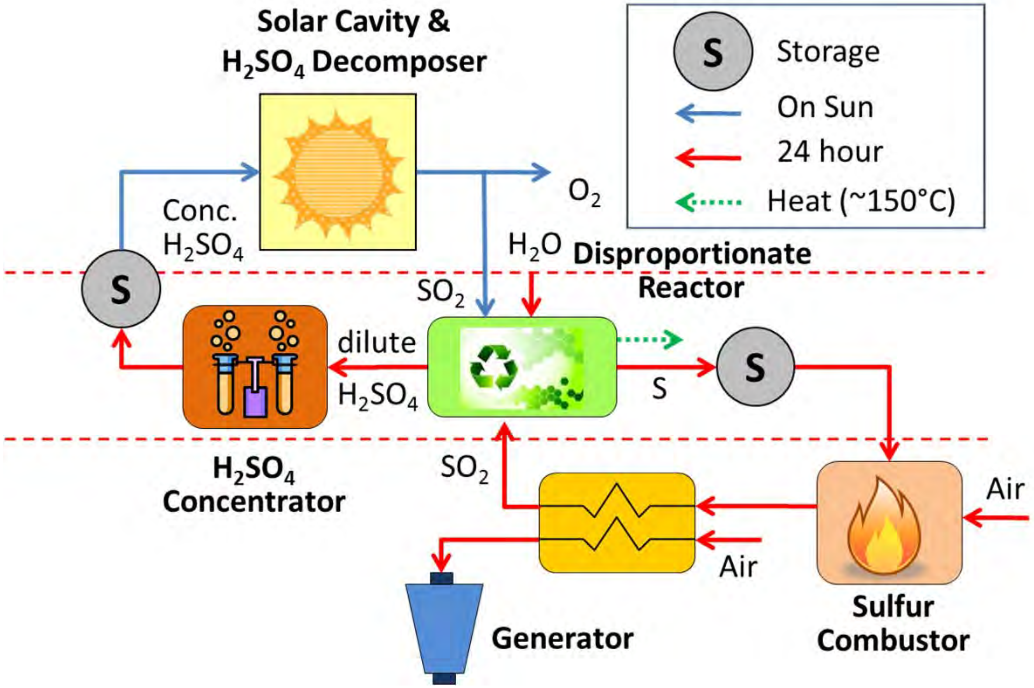
(Summary)

Sulfur based



	Reaction	Temp (° C)
H_2SO_4 Decomposition	$2H_2SO_4 \rightarrow 2H_2O(g) + O_2(g) + 2SO_2(g)$	800
SO_2 Disproportionation	$2H_2O(l) + 3SO_2(g) \rightarrow 2H_2SO_4(aq) + S(l)$	150
Sulfur Combustion	$S(s,l) + O_2(g) \rightarrow SO_2(g)$	1200

Preliminary economics was assessed using a process flowsheet

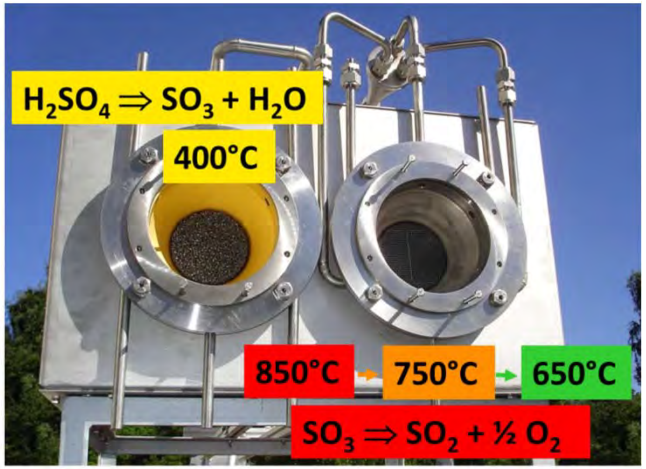


- *maximizes solar capacity*
- *economical diurnal and seasonal energy storage*
- *constant daily/ year round power supply*
- *Brayton* or *combined* cycle
- *environmentally friendly*

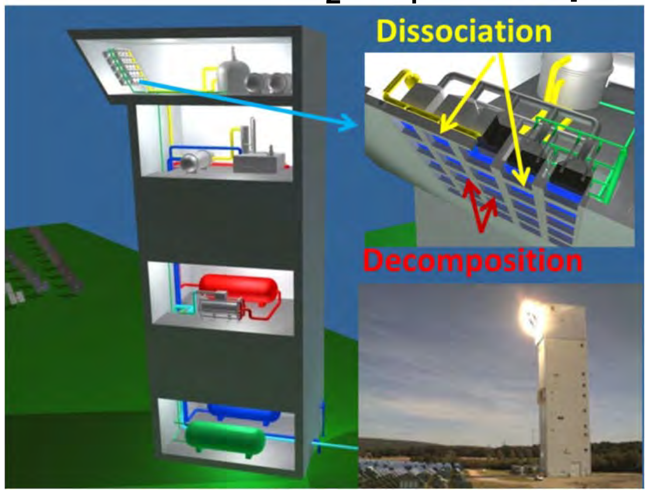
DOE Metric	Capacity Factor	LCOE (¢/kWh$_e$)
DOE Targets	75%	6.5
CSP w/Sulfur Storage	>75%	8.7*

*SAM (NREL) using 2010 costs

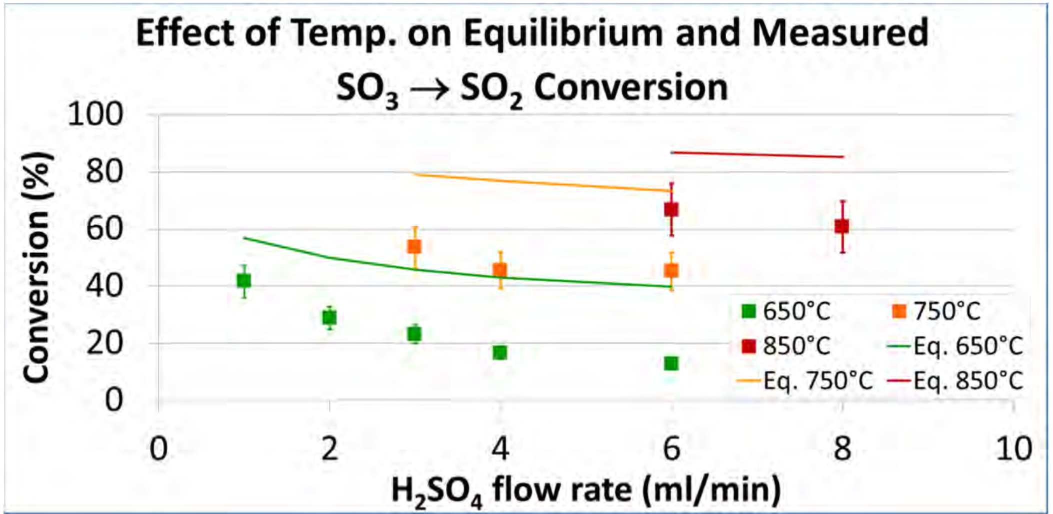
Sulfuric acid decomposition on sun using a solar furnace



A dual chamber H_2SO_4 decomposer



Conceptual scale up of a modular decomposer on a solar tower

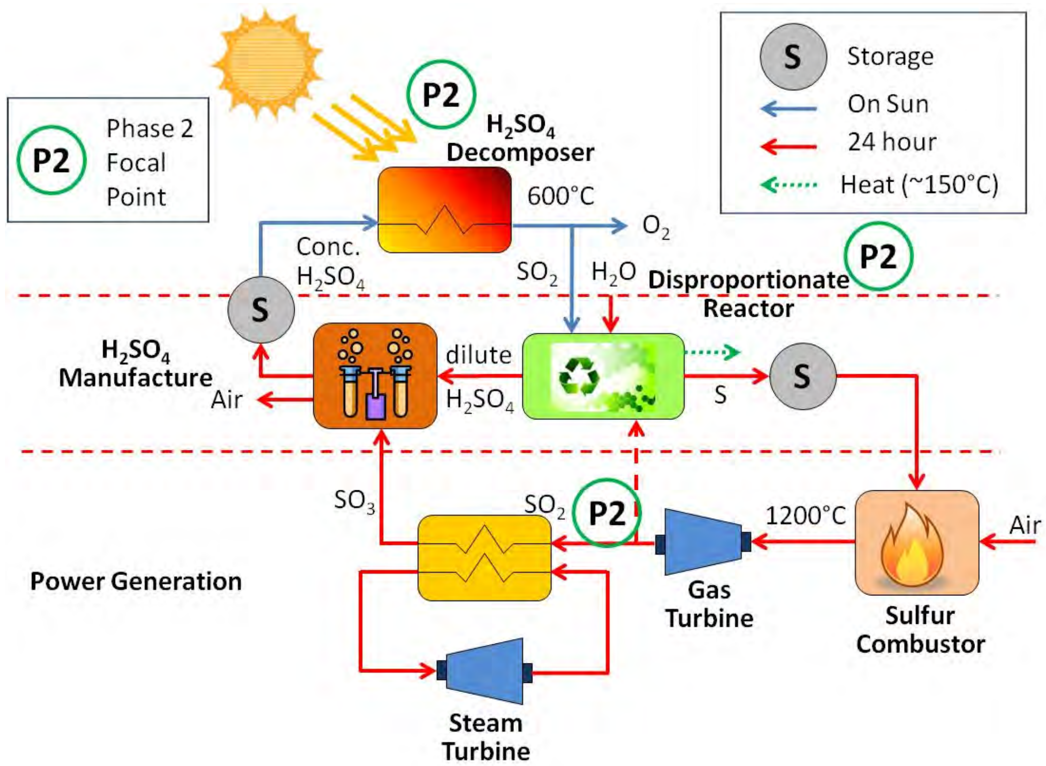


- **Process and decomposer refinement based on test data**
- **Lower decomp. temperature to reduce solar installation cost**

D. Thomey et al., Int. Journal of Hydrogen Energy (2012)

An improved flowsheet was established based on modeling and experimental data from Phase I

- **Plant design incorporated established processes from sulfuric acid manufacturing plant**



DOE Metric	LCOE (¢/kWh$_e$)
DOE Target	6.5
CSP w/Sulfur Storage	8.1*

***SAM (NREL) using 2012 costs**

- **Storage cost is < $2/kWh**
- **LCOE is ~6¢/kWh$_e$ based on proposed Sunshot targets**

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Summary and Outlook

- **Thermo-Chemical Energy** storage
  - Has a high potential for the future energy economy as well for Germany as stated in the 6th ERP as for the EU which just implements it in the HORIZON 2020 framework
  - DLR will contribute to these efforts

  - **Technically it offers several advantages** like
    - potentially high storage density,
    - lossless long-term storage

  - **the crucial points are**
    - adapted reactor systems and
    - process integration

Acknowledgement

- Thanks to all our funding agencies especially the European Commission and our industrial partners.

- Thanks to all colleagues and partners who provided various contributions to this work.

DLR H_2 Aircraft
ANTARES

Thank you very much for your attention!